

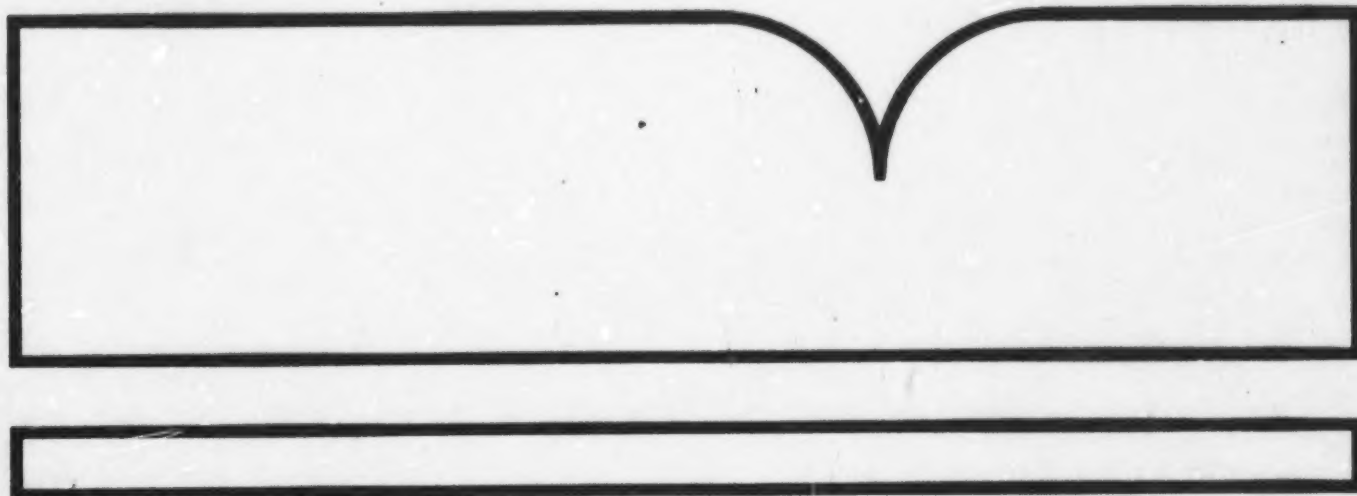
The Development of Potential Thin Standards for
Calibration of X-Ray Fluorescence Spectrometry

(U.S.) National Bureau of Standards
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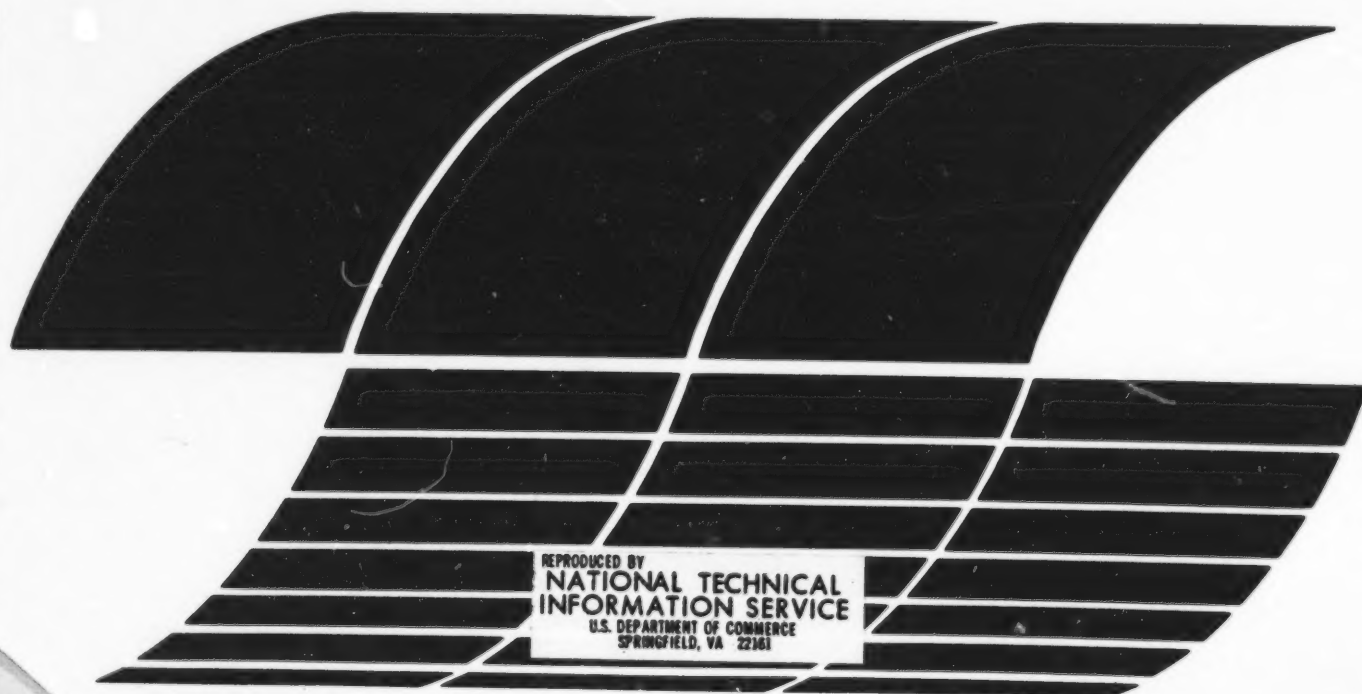
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THE DEVELOPMENT OF POTENTIAL THIN STANDARDS FOR
CALIBRATION OF X-RAY FLUORESCENCE SPECTROMETRY

by

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FOREWORD

The role of the National Bureau of Standards (NBS) in the Interagency Energy/Environment R&D program, coordinated by the Office of Research and Development, U. S. Environmental Protection Agency, is to provide those services necessary to assure data quality in measurements being made by a wide variety of Federal, State, local, and private industry participants in the entire program. The work at NBS is under the direction of the Office of Environmental Measurements and is conducted in the Center for Analytical Chemistry, the Center for Radiation Research and the Center for Thermodynamics and Molecular Science. NBS activities are in the Characterization, Measurement, and Monitoring Program category and addresses data quality assurance needs in the areas of air and water measurement methods, standards, and instrumentation. NBS outputs in support of this program consist of the development and description of new or improved methods of measurement, studies of the feasibility of production of Standard Reference Materials for the calibration of both field and laboratory instruments, and the development of data on the physical and chemical properties of materials of environmental importance in energy production. This report is one of the Interagency Energy/Environment Research and Development Series reports prepared to provide detailed information on an NBS measurement method or standard development.

William H. Kirchhoff, Chief
Office of Environmental Measurements
National Bureau of Standards

ABSTRACT

Thin films containing known concentrations of metals are important for the calibration of X-ray Fluorescence Spectrometry (XRF), especially for the analysis of collected airborne particulate matter. A focused ion-beam sputtering technique has been investigated as a candidate method for fabricating thin glass films containing known concentrations of metals on polycarbonate substrates. Glass targets were fabricated at NBS for these studies, and parameters such as ion-acceleration voltage and ion current were systematically varied to determine any changes in film composition. It was found that rather severe changes in instrumental parameters do not affect the elemental composition of the films appreciably. Up to eight substrates were coated at one time and the compositional reproducibility as measured by XRF for Si, Ca, Zn, and Pb for 13 samples was within five percent relative standard deviation at mass loadings of glass from 160 - 190 $\mu\text{g}/\text{cm}^2$. Glass films containing phosphorous and sulfur were also prepared to demonstrate the feasibility of preparing glass films containing such elements of low atomic number. Additional studies consisted of the deposition of finely ground synthetic glasses on membrane filters, and the characterization of some selected commercial thin films prepared by thermal evaporation.

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SECTION 1

INTRODUCTION

X-ray fluorescence spectrometry has proven to be a versatile and rapid method for multielement analysis in many analytical applications. Of particular interest are substances which can be analyzed in the form of a deposit on a filter, mesh or membrane, or as a thin pressed pellet. Collected airborne particulate matter, particulates in waste water and geochemical samples are just a few examples of this type. In some respects such "thin samples" are ideal for x-ray fluorescence analysis because the detection limits are suitably low and interelement effects such as x-ray absorption and/or enhancement are negligible. The absence of any sizable interelement effects makes possible a linear instrument response to element mass per unit area. Some problems associated with the "thin specimen model" are x-ray self-absorption in particles notably for the light elements such as Al, Si, P, and S commonly referred to as particle-size effects, and self-absorption in the substrate. Both of these effects require the application of correction factors. Therefore, the basic premise is that accurate multielement analysis of thin samples can be performed based on the thin specimen model, together with empirical or theoretical correction factors.

For a thin specimen the count rate I_1 of characteristic x-rays from an element i is linearly related to the element mass per unit area, m_1 (g/cm²):

$$I_1 = S_1 m_1 \quad (1)$$

where S_1 is the sensitivity or calibration factor for element i , and is in units of counts/s per $\mu\text{g}/\text{cm}^2$. S_1 is usually determined experimentally with thin standard samples. A thin specimen is arbitrarily defined as one having a total mass per unit area given by*

$$m = \frac{0.1}{\bar{\mu}} \quad (2)$$

where the effective, average mass absorption coefficient $\bar{\mu}$ in cm²/g is

$$\bar{\mu} = \mu_1 \text{ cosec } \theta_1 + \mu_2 \text{ cosec } \theta_2 \quad (3)$$

*assumes x-ray photon excitation

where μ_1 is the sample mass absorption coefficient for the primary radiation energy, μ_2 is that for the characteristic x-ray energy, and θ_1 and θ_2 are the glancing angles of incidence and emergence, respectively. The deviation from linear response due to sample self-absorption is approximately equal to 0.5 μm . This so-called critical thickness is a good guide to determining sample "thinness" and can be estimated from equation 2.

There are several types of "thin" samples presently available from commercial sources (1,2) which are used to calibrate x-ray spectrometers. These generally consist of:

(1) Thin films of single metallic elements deposited by thermal evaporation on mylar or thin aluminum substrates. The mass loading is usually determined by the manufacturer using gravimetry.

(2) Dried solution deposits on membrane filters. These are prepared by a multi-drop technique where ten or more elements are present in concentrations ranging from 1 to 50 mg/cm^2 as stated by the manufacturer.

(3) Synthetic particulate deposits consisting of previously characterized rock samples ground and dispersed on membrane filters and fixed to the filter with a 30-40 mg/cm^2 layer of paraffin wax.

In addition to commercial sources, a number of workers have reported on techniques for preparing thin standard specimens (3-11). Pella et al. (3) reported on a technique for depositing a reground NBS-Standard Reference Material (NBS-SRM 1571 Orchard Leaves) on membrane filters and coated with vapor-deposited Parylene films. Baum et al. (6) described a capillary matrix and lyophilization procedure for preparing solution deposited standard samples. Dzubay et al. (9) have developed calibration samples consisting of polymer films each containing a single calibration element. The film is cast from a homogeneous solution containing known amounts of an organometallic compound and a polymer. Olson et al. (10) used an air filter calibration facility for preparing standard samples. Recently, Semmler et al. (11) describes a technique where micron sized particles of known compounds suspended in a carrier solution are deposited onto the surface of a Nuclepore filter. Particle size is controlled by a separate sedimentation step following grinding in a boron carbide mortar and pestle. Binding of the deposit to the filter is accomplished with collodion film.

There are several important criteria which need to be met if thin specimen samples are to be acceptable for calibration purposes. First, the uniformity of the sample as well as its homogeneity must be within an acceptable well-defined tolerance limit. If the sample contains particulate matter, both the size and distribution should be characterized. Secondly, the mass loading of the sample must be known to an acceptable degree of accuracy. And finally, the sample should possess sufficient durability and integrity. The goal of the NBS-EPA XRF program is to perform the research and development required to produce thin standard samples especially useful for calibration of x-ray fluorescence analysis of collected airborne particulate matter. For this purpose we have investigated candidate methods for preparing such samples and the results are summarized in this report. These consist of (a) the deposition of

thin glass films on polycarbonate substrates by focused-ion beam sputtering (12-15), (b) the deposition of NBS-SRM 1648 urban particulate on membrane filters, and (c) the deposition of finely ground synthetic glasses on membrane filters. In addition, we have also characterized some selected thin films from a commercial supplier prepared by thermal evaporation to assess the state-of-the-art for some types of thin films. The sputtering experiments described in this report were performed initially with the model MIM/TLA 5.5 instrument, and subsequent work with the larger MIM/TLA 15 system.

SECTION 2

EXPERIMENTAL PROCEDURES

1. FOCUSED-ION BEAM SPUTTERING

Ion sputtering is essentially a technique which involves the transfer of molecules from a target to a substrate by the action of an ion beam incident upon the target as shown in Figure 1. The ion gun is of the field accelerated design. Permanent magnets cycloidally accelerate electrons thermally emitted from a double-filament thoriated tungsten electrode (see Figure 2). These electrons produce ionization of an inert gas, usually argon, thus creating a high intensity plasma. The argon ions are extracted from the plasma and accelerated at the target using optically aligned molybdenum grids. The resulting 15 cm diameter ion beam is neutralized using an immersion flood neutralizer. The neutralized ion beam is further collimated to about 12 cm with a baffle plate coated with high purity aluminum oxide to reduce contamination of the sputtered film due to the container walls. The ion beam is accelerated at high potential from 700-1100 volts at a flux of 0.5 mA/cm^2 toward the target at a 45° angle. Since the substrate is not in the plasma environment, substrate damage does not occur and is a distinct advantage of this particular sputtering technique. Also, operating parameters such as deposition rate, angle of deposition, and temperature which can effect thin film properties can be varied easily and independently. The sputtered material is deposited at a relatively low energy, typically 100 eV, so that no impact damage to the substrates result. To ensure deposits of high purity the system is operated at low pressure (10^{-5} mm Hg range). The main advantages to be gained by using such a technique appear to be as follows:

- (1) Production of standard thin films from synthetic materials such as glasses with known elemental composition which can be varied as desired.
- (2) High adherences of the films to the substrate which obviates the need for adhesive materials to maintain the standard material on the substrate.
- (3) Easy control of the mass loading on the substrate by variation of the sputtering time.

2. STUDY OF POLYCARBONATE SUBSTRATES

Membrane filter materials such as Millipore and Nuclepore are finding increasing use as substrates for preparing samples for x-ray fluorescence analysis. This is because these materials have relatively low levels of trace

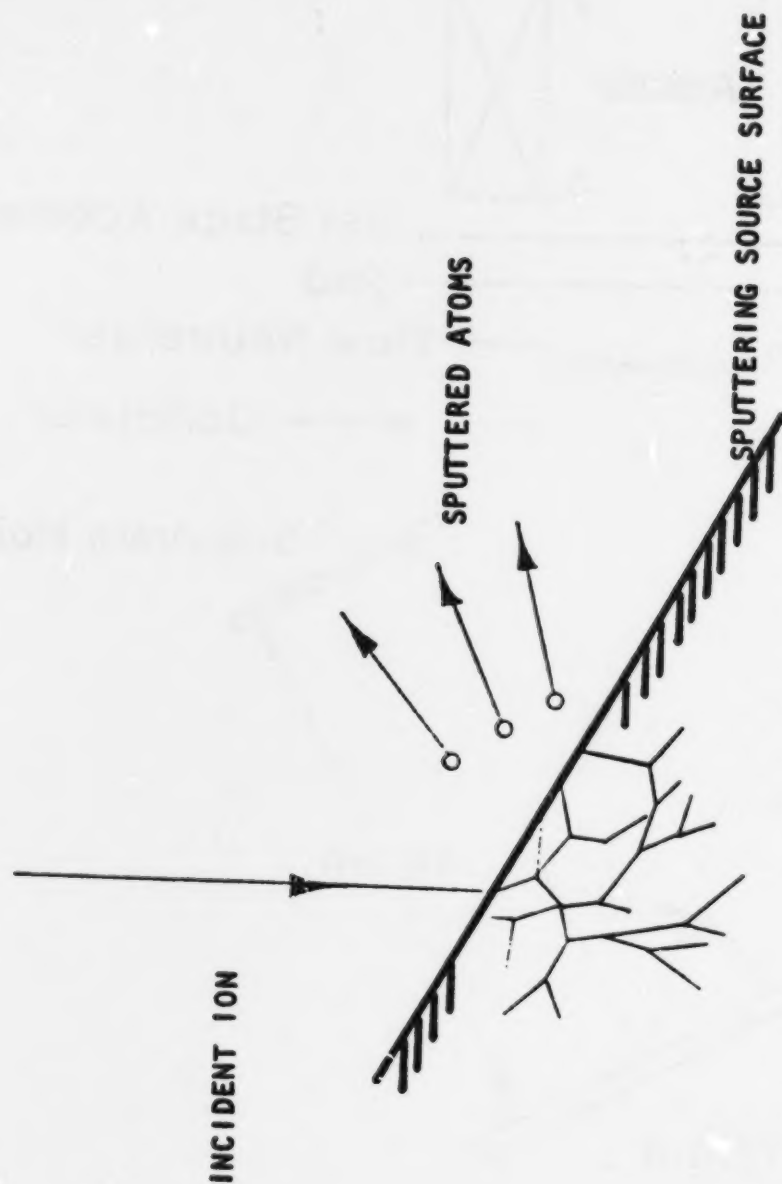


Figure 1. Cascade collision resulting in sputtering.

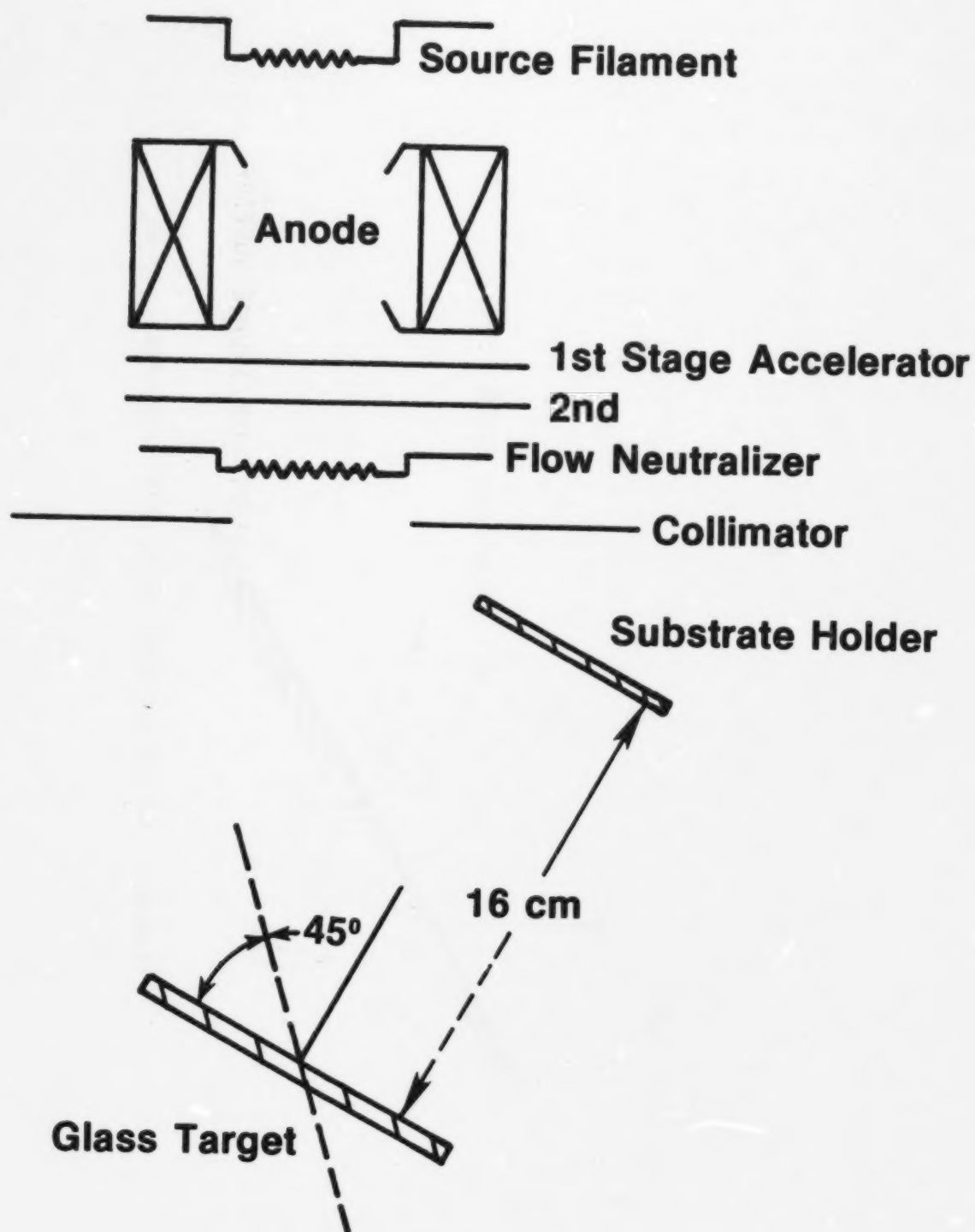


Figure 2. Schematic diagram of sputtering apparatus.

elements and their mass is quite low (e.g. on the order of 1 mg/cm^2). Nuclepore is a polycarbonate material which has quite distinct advantages over Millipore in that it contains lower concentrations of trace elements such as Cl and Fe and is more durable under x-ray photon bombardment. We have checked the purity and measured the effects of humidity on polycarbonate material. The need to assess the effect of humidity is important in order to use gravimetry for measuring the mass loading of the films. Examination of the polycarbonate by energy-dispersive x-ray spectrometry (EDXRF) revealed detectable amounts of Ca and Fe. However, these concentrations are believed to be at levels sufficiently low not to cause any blank problems.

A number of Nuclepore polycarbonate filters were weighed to $.001 \text{ mg}$ in a constant humidity environment ($55 \pm 1\%$ relative humidity) and at room temperature $24 \pm 1^\circ \text{C}$. Variations in the weight of each filter were on the order of $\pm 0.005 \text{ mg}$ which was a little less than 0.1 percent of the total mass of the filter. The first study of humidity effect was done by exposing a number of filters to 100 percent relative humidity environment for two days and then removing these and immediately reweighing them in 50 percent relative humidity environment. The weights were recorded periodically over a time span of about four hours. After about ten minutes the filter weights were in agreement within 0.1 percent of the original weights of the filters.

A second study was performed in a similar manner by placing preweighed filters in an 11 percent relative humidity environment for two days and reweighing them after ten minutes in the 50 percent relative humidity environment. Again the filter weights were within 0.1 percent agreement with these preweighed values. These studies showed that these filters quickly reached equilibrium with the environment in which they were weighed and indicated that changes in humidity do not cause any serious problems.

3. SYNTHESIS OF GLASS TARGETS

Synthetic glasses were selected for producing thin films because these materials can, in principle, be fabricated containing various elements of interest at desired concentration levels. Several glass disks were prepared by D. Blackburn and D. Kaufmann of the NBS Inorganic Glass Section. In the initial studies performed with the MIM/TLA 5.5 instrument, glass disks 7.6 cm in diameter were fabricated. For work with the model MIM/TLA 15 glass targets 17.8 cm in diameter were cast. The nominal composition of the glass targets is summarized in TABLE 1.

TABLE 1. NOMINAL COMPOSITION OF GLASS TARGETS (A-D) FABRICATED AT NBS

Compound	Wt. %			
	A	B	C	D
SiO ₂	36.0	36.0	45.0	--
Al ₂ O ₃	13.5	--	--	--
Fe ₃ O ₄	13.5	--	--	--
CaO	18.0	18.0	--	--
MgO	9.0	--	--	--
K ₂ O	10.0	--	--	--
ZnO	--	20.0	--	--
PbO	--	26.0	--	--
Na ₂ SO ₄	--	--	20.0	--
Na ₂ O	--	--	35.0	--
Al(PO ₃) ₃	--	--	--	70.0
NaPO ₃	--	--	--	30.0

The constituents for target A were fused at 1511 °C for three hours in a Pt crucible with continuous stirring. The melt was cast into a 7.6 cm diameter mold on a preheated hot plate and then annealed at 685 °C for ten minutes and then allowed to cool to room temperature. Target B constituents were fused at 1400 °C, and poured into molds (7.6 and 17.8 cm) at 1200 °C, and annealed overnight at 650 °C. Fusion and annealing temperatures for targets C and D (17.8 cm) were 1225 °C and 420 °C, and 1300 °C and 525 °C, respectively. For casting targets in the 17.8 cm mold about 700-900 g of glass was melted. The glass target surface was first coarsely ground on a diamond disk (220 grit) then polished with 22.5 μ Al₂O₃, then 9.5 μ, and finally 0.5 μ sapphire. The 17.8 cm disks were all ground to a thickness of 0.3 cm. The homogeneity of the target A surface was studied to at least a depth of 2 μm by scanning electron microscopy fitted with a Si (Li) detector. The electron beam was scanned across at least 25 different points on the target, and the characteristic x-rays of Mg, Al, Si, K, Ca, and Fe were measured. The results indicated that the target was homogeneous within the Poisson counting statistics error of 1-2%. Targets B, C, and D were examined by EDXRF and were found to be homogeneous with respect to elemental content within 3%.

4. INITIAL EXPERIMENTS

Initial experiments were designed to obtain information on sputter rate and the cleanliness of the ion-beam sputtering apparatus which was used. Since this machine (model MIM/TLA 5.5) was used primarily for demonstration purposes, and was in almost continuous operation for producing films of several elements, the sputter gun was disassembled and was cleaned thoroughly before sputtering our targets. A disk of high-purity SiO_2 was sputtered for five hours on one polycarbonate substrate and the resulting SiO_2 film was examined by x-ray fluorescence. The main impurities found were Fe, Mn, Cr and Ni, which were attributed to the sputtering of the stainless steel ion current monitor by the primary beam. A small amount of Al contamination arose from sputtering of the walls of the ion gun. Four deposits of the synthesized glass target A were sputtered for various times to obtain information on the sputter rate and to determine the length of time necessary to obtain a film of adequate thickness to provide good x-ray counting statistics for the XRF measurements. In Figures 3 and 4 are xrf spectra of the glass target A and film, respectively. From these experiments it was determined that under a particular set of machine operating parameters, films from 100 to 400 $\mu\text{g}/\text{cm}^2$ could be deposited in 4 to 16 hours. The sputtering time could be shortened by using higher beam currents but it was found that considerable heating of the polycarbonate substrates occurred with resultant damage. Henceforth, machine operating conditions were deliberately chosen so that the substrate temperature did not exceed 80 °C. Temperature studies of the polycarbonate substrate filters (37 mm diameter) showed that cycling temperatures from 25 to 80 °C did not change the weight of the filters when remeasured at room temperature. It was also found that the glass-coated polycarbonate substrates tended to wrinkle when removed from the substrate holder. This made it extremely difficult to remount in a flat reproducible configuration for xrf measurements. For this reason an aluminum ring holder was constructed to maintain the substrates flat as shown in Figure 5. The assembly could then be transferred directly to our xrf instrument for measurement. Both Teflon and aluminum insert rings were made for use in order to keep the substrate in a stretched state in its aluminum ring holder. The Teflon insert ring was especially useful when the glass-coated substrate needed to be demounted for weighing to measure the mass of the glass deposit.

To reduce the Fe and Cr contamination from the sputtering system, the stainless steel ion current monitor was wrapped with Al foil and all surfaces in the system where possible sources of contamination could arise were lined with Al foil. Because the substrate holder in the system was made to accommodate only one sample at a time, another holder was constructed at NBS to accommodate three samples at one time which rotated when the glass films were being deposited. A high purity SiO_2 target was then sputtered for 720 minutes to provide three samples. The films were removed and examined for impurities by energy-dispersive xrf using a Ni secondary emitter for excitation. The resultant intensities were compared with a blank substrate tabulated in TABLE 2. As seen from the table, appreciable amounts of Al, Ar, and Fe appear in the sputtered SiO_2 films. The Ar contamination arises from the argon entrapped in the glass during the sputtering operation.

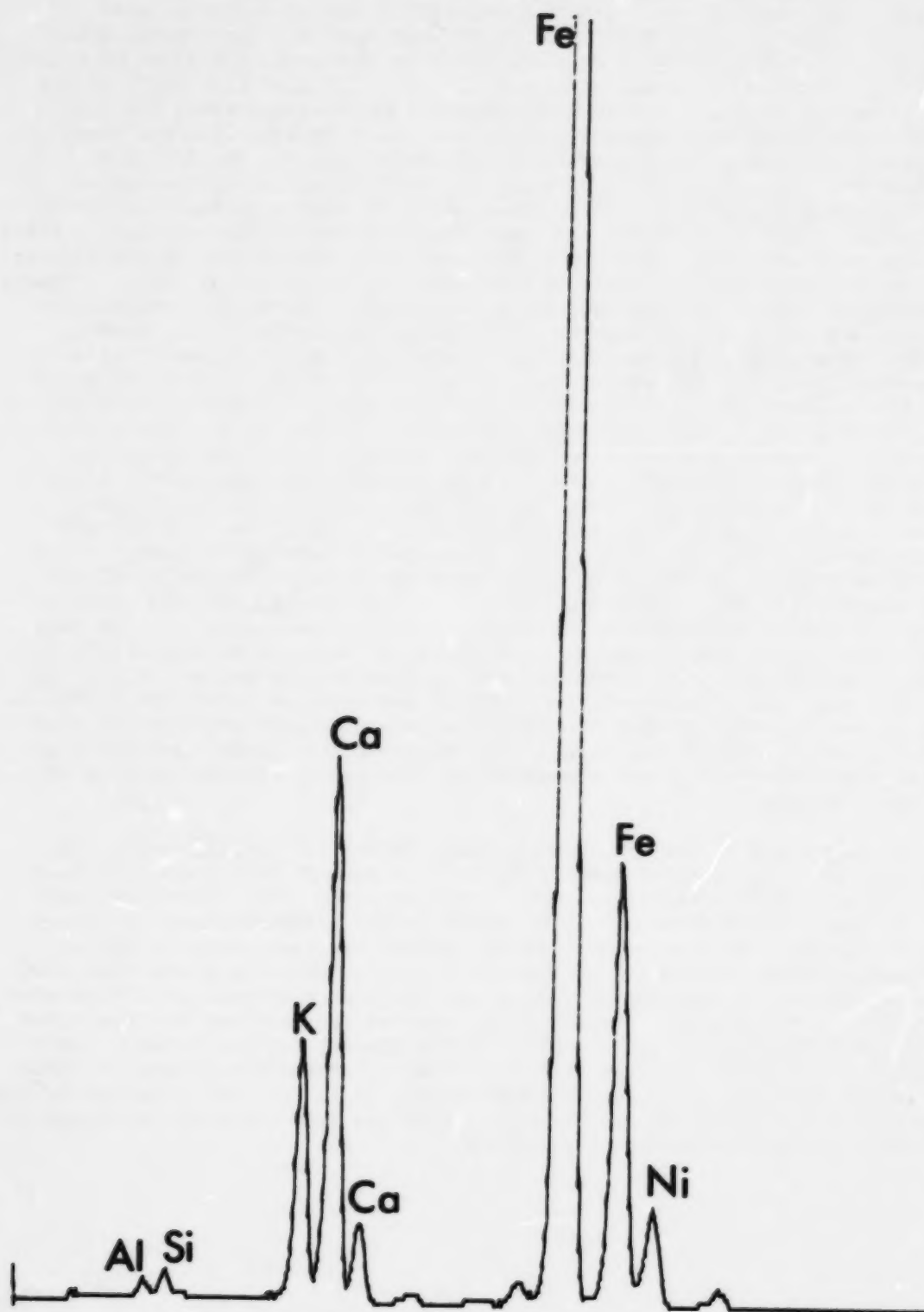


Figure 3. X-ray fluorescence spectrum of glass target A.

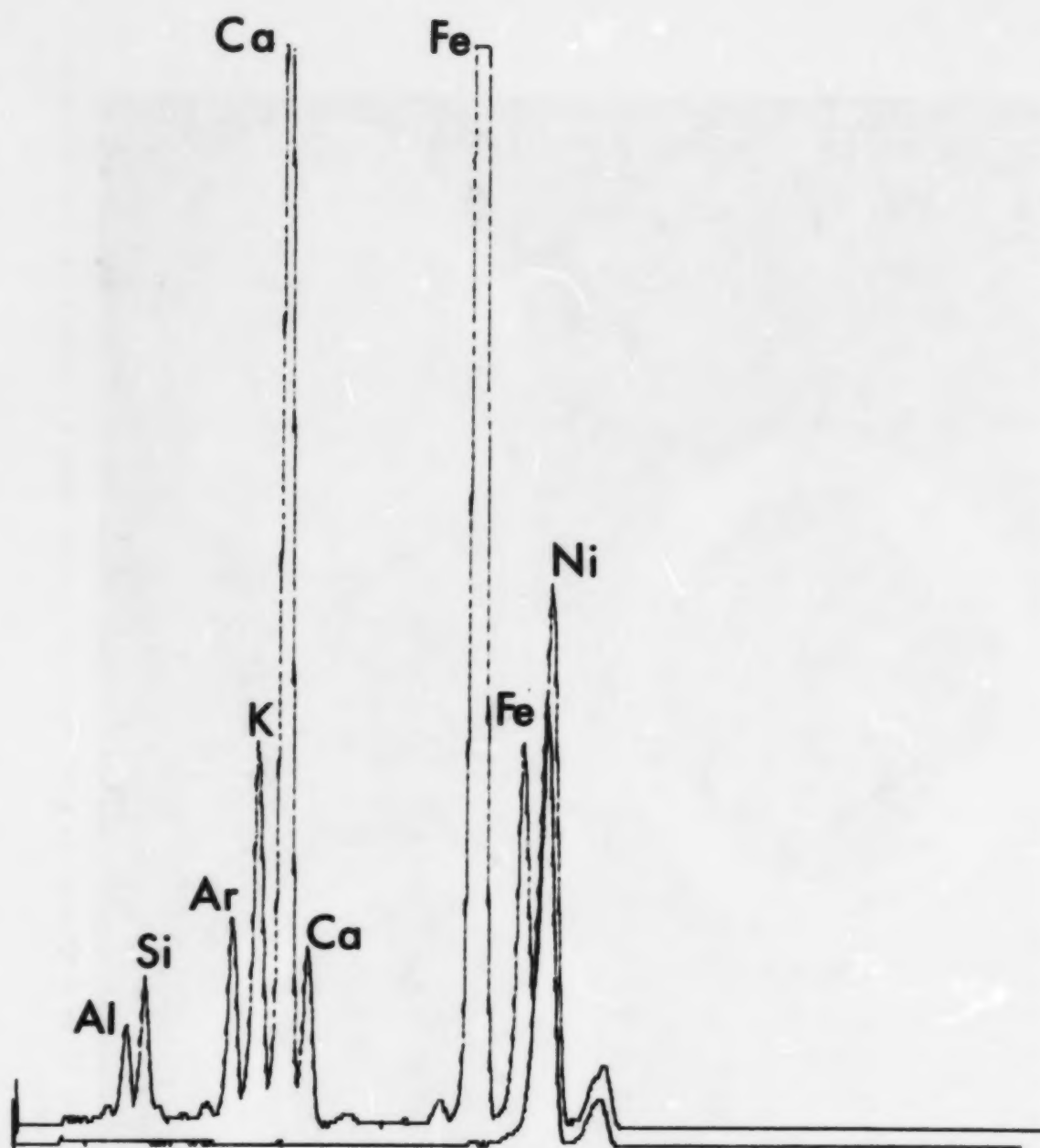


Figure 4. XRF spectrum of sputtered glass film (target A).

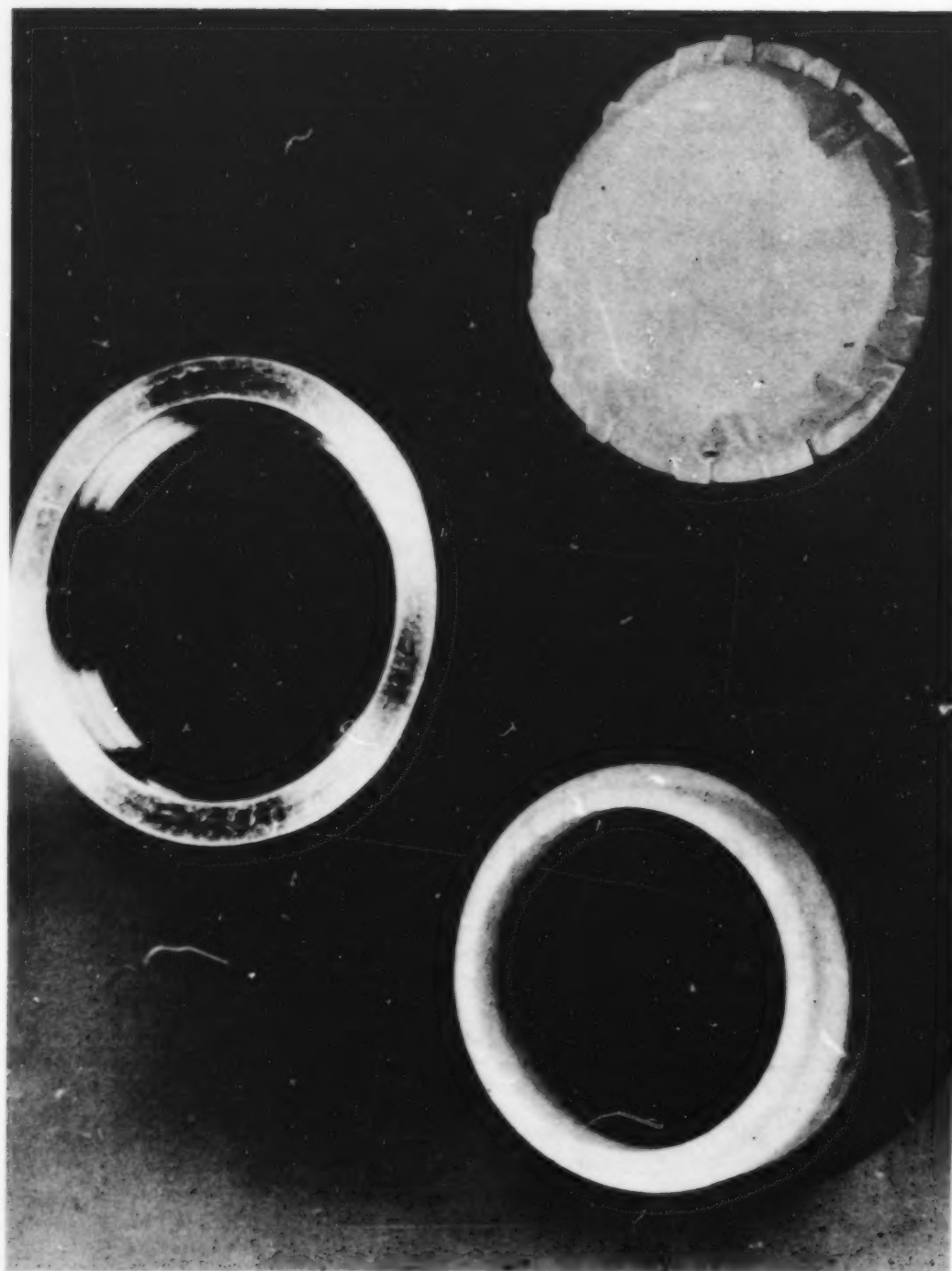


Figure 5. NBS holder for 3/ mm polycarbonate substrates. A = outer ring; B = inner ring; C = polycarbonate substrate.

TABLE 2
ELEMENT X-RAY INTENSITIES FROM SPUTTERED SiO₂ FILMS COMPARED WITH
A BLANK POLYCARBONATE SUBSTRATE (MIM/TLA 5.5)

Film	Gross Counts (Average) in 1000 Seconds					
	Al	Si	Ar	K	Ca	Fe
SiO ₂ #1	16,134	186,412	28,131	3,847	939	14,724
SiO ₂ #2	17,494	179,072	27,936	3,978	1,019	14,903
SiO ₂ #3	14,188	178,212	26,944	3,853	941	14,645
Blank	2,098	1,391	1,474	1,212	1,451	1,834

XRF Conditions: 45 KV, 30 MA, Ni secondary emitter, in vacuum

To get an estimate of the radial uniformity of the sputtered glass film seven 1 X 1 cm vitreous carbon squares were distributed between and around two polycarbonate substrates on the substrate holder. The glass target A was then mounted and sputtered for 20 hours onto each of the polycarbonate substrates and the seven carbon squares. This gave a film approximately 400 µg/cm². The films on five of the carbon substrates were examined by SEM using a Si (Li) x-ray detector. The K_α x-ray intensities of Al, Si, K, Ca, and Fe were measured on each of the carbon squares and were found not to vary by more than 3% of the measured x-ray intensity.

To obtain information on the mass loading of the glass films with time of sputtering, three sets of three substrates each were glass coated for 180, 360, and 540 minutes, respectively, and the x-ray intensities were measured by EDXRF. A summary of this data is presented in TABLE 3. As seen from the table, the mass loading of the film does increase approximately in proportion to the sputtering time.

The results of these preliminary studies indicated that glass targets appeared to be suitable for producing thin standards by this technique. The uniformity of these films were acceptable. Several problems, however, did arise as a result of these studies. First, elemental contamination of the films from the sputtering environment was significant. Secondly, target heating became appreciable during ion bombardment and also caused localized heating of the substrates with some apparent damage. Also, the instrument used could not accommodate more than three substrates at one time which was clearly unsatisfactory. These problems were overcome with the advent of the larger Model MIM/TLA 15 instrument which became available to us in 1978 (see Figures 6 and 7). The main features of this larger instrument are summarized as follows:

TABLE 3. X-RAY INTENSITY DATA FOR VARIOUS ELEMENTS VS. SPUTTERING TIME
(TARGET A)

Sputtering Time, min.	Sample	Al	Si	Ar	K	Ca	Fe
180	1	17,169	23,791	42,511	80,734	293,873	643,062
	2	16,440	23,000	39,939	78,267	283,927	620,588
	3	17,567	25,341	44,436	84,688	308,935	687,640
	Average	= 17,059	24,044	42,295	81,230	295,578	650,430
	Rel. Std. Dev.	= 3.4%	5.0%	5.3%	4.0%	4.3%	5.2%
360	1	25,381	34,762	71,986	128,505	485,841	1,031,281
	2	25,855	33,073	72,956	124,147	481,355	989,017
	3	26,089	34,760	74,745	130,598	495,574	1,044,297
	Average	= 25,775	34,198	73,229	127,750	487,590	1,021,532
	Rel. Std. Dev.	= 1.4%	2.8%	1.9%	2.6%	1.5%	2.8%
540	1	36,568	42,304	119,766	156,215	748,193	1,328,058
	2	36,211	40,907	119,502	151,758	733,963	1,271,554
	3	37,659	43,825	127,401	163,889	784,836	1,385,397
	Average	= 36,813	42,345	122,223	158,287	755,664	1,328,336
	Rel. Std. Dev.	= 2.0%	3.4%	3.7%	3.9%	3.5%	4.3%

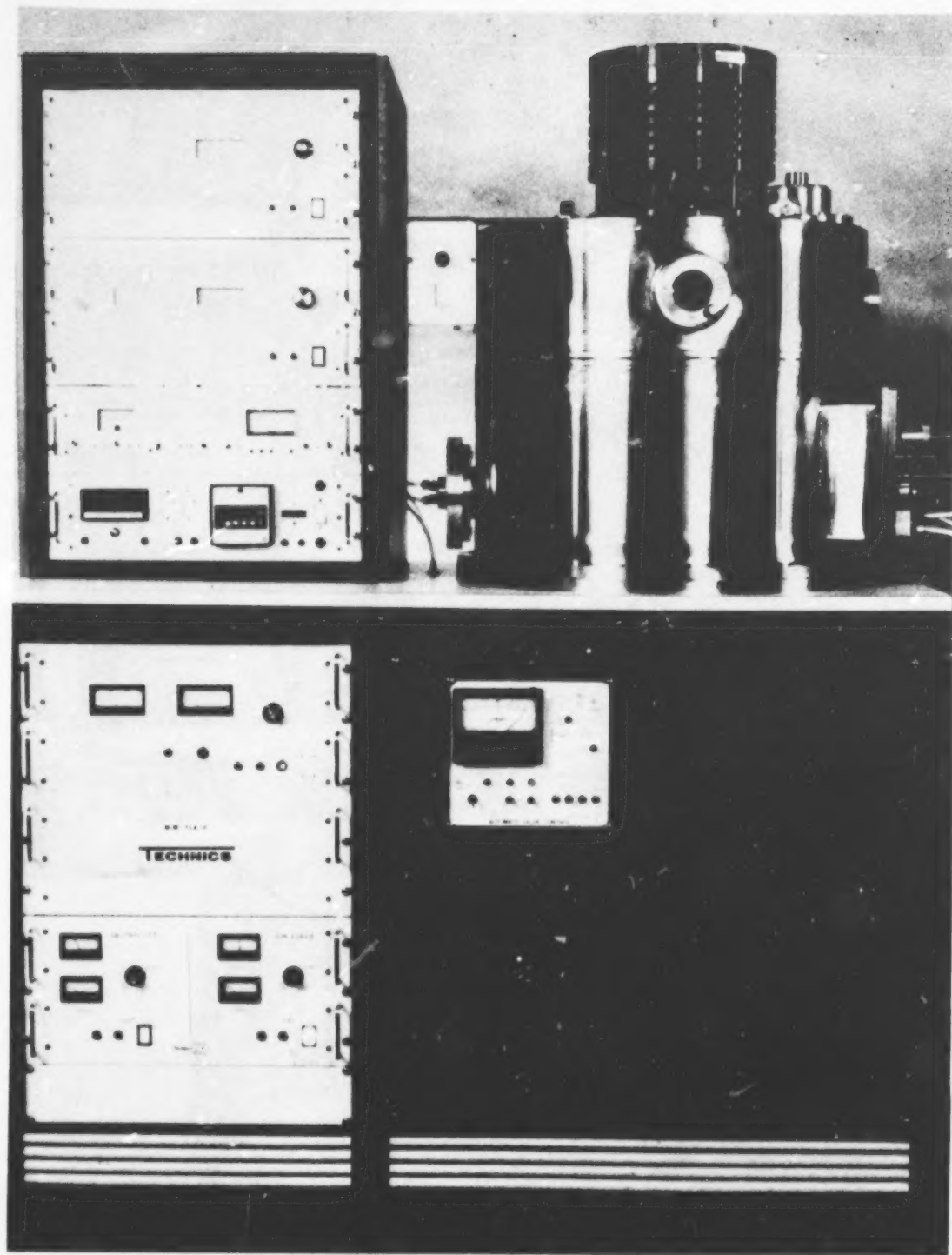


Figure 6. Model MIM/TLA15 (front view).

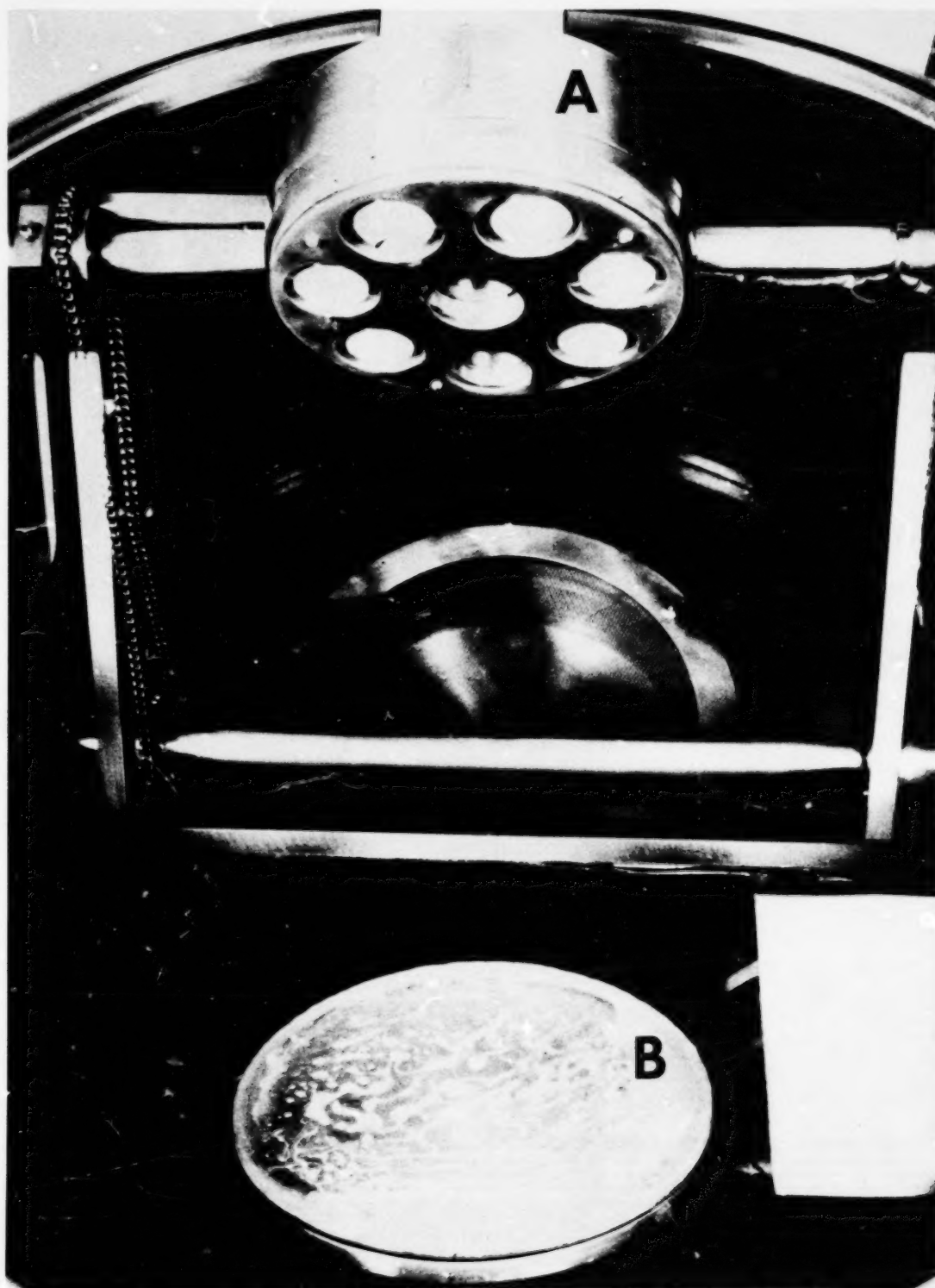


Figure 7. View into chamber of MIM/TLA 15. A = rotating substrates; B = glass target.

(1) The substrate stage (15.24 cm in diameter) was water cooled, rotatable at 1 RPM, and allowed up to eight (37 mm diameter) substrates to be coated simultaneously.

(2) The angle of beam incidence was variable from 0°-180°.

(3) The target holder was a 15.24 cm diameter water-cooled stainless steel plate.

(4) The stainless steel chamber which housed the target and substrate assemblies was 61 cm in diameter which allowed for easier loading and removal of samples.

These features allowed more samples to be coated simultaneously without any significant buildup of heat in the system. We needed, however, to fabricate larger glass targets to accommodate the 15 cm diameter ion beam. For this purpose, we cast 17.8 cm glass disks. To obtain efficient heat transfer through the glass, the target was ground and polished to a thickness of 0.3 cm by the NBS glass section. An aluminum plate was fabricated in order to heat sink the glass plate to the water-cooled target stage. Binding of the glass target to the aluminum plate was accomplished with a flexible silver-filled epoxy (17). A substrate holder was also made at NBS to perform simultaneous glass deposition on eight 37 mm substrates. Again experiments were performed using a pure SiO_2 target to assess any elemental contamination of the sputtered film. To eliminate contamination we found it necessary to further minimize any interaction of the incident beam with the sides and bottom of the chamber. For this reason we fabricated an aluminum baffle plate placed between the beam and the glass target in order to collimate the beam diameter to 12.7 cm. Although effective collimation was obtained, we found considerable elemental contamination produced from the collimation plate itself. This problem was eliminated by coating the collimator plate with 99.99% Al_2O_3 by a flame-spraying technique. Subsequent experiments with a SiO_2 target showed detectable amounts of aluminum and copper in the SiO_2 films but at blank levels that were acceptable.

5. GLASS FILM COMPOSITION STUDIES A

The elemental composition of glass films produced from targets A and B was determined by EDXRF and by electron probe microanalysis and compared to the bulk glass composition of the targets. Standards used for the XRF calibration consisted of: (a) reground NBS-SRM 1571 orchard leaves on membrane filters (3), (b) thin films of zinc and lead produced by thermal evaporation of the metals, and (c) SiO_2 on polycarbonate prepared by sputtering high purity quartz. Ti, Ni, and Mo x-ray targets were used to produce monochromatic excitation of the samples. The conditions used for the XRF analysis are summarized in TABLE 4.

TABLE 4. X-RAY CONDITIONS USED FOR ELEMENT ANALYSIS^a

Elements Analyzed	W tube	Exciter	Vacuum
Si, K, Ca	45 KV, 30mA	Ti	Yes
Pb,Zn	45 KV, 30mA	Mo	No
Fe	20 KV, 30mA	Ni	Yes

^a Analysis time was 1000 seconds.

For microprobe analysis, a square piece of a sputtered glass film (F-1035) was mounted on a flat, polished vitreous carbon square (1 cm x 1 cm) and was placed next to a small slice of the glass target so that the surfaces were coplanar. The specimen was then prepared for electron probe microanalysis in a conventional manner. The electrons were accelerated at 10 KV to produce a probe 10 μ m in diameter. The range of an electron beam of this energy was calculated to be about 1.2 microns for a silicate material. The mass of the sputtered glass film was about 400 μ g/cm² and approximately 2 micrometers thick. The results of the x-ray analyses of the thin films prepared with the model MIM/TLA 5.5 instrument are given in TABLES 5 and 6 for each of the glass targets used. The first column in each table indicates the time sequence in which the glass films were prepared. The nominal compositions of the respective glass targets are included in the tables for comparison. Examination of the results shown in TABLE 5 (target A) indicate that the CaO content of the films appears to be the same from sample-to-sample and close to the nominal composition of the bulk glass at 18.0 percent. Greater variation in concentrations was noted for K and Fe, which were significantly below the nominal values. The SiO₂ composition appeared to be close to the nominal value only in those films which were sputtered for the longest times, F-1035 (17 hrs) and F-7 (9 hrs). From the results in TABLE 6 (i.e., target B) little variation in the CaO content of these films was noted, but almost twice the nominal value was obtained. The PbO to ZnO ratio in the films was comparable to the ratio in the bulk glass but the absolute values of the concentration were very low compared to the nominal values. The results of the electron microprobe analysis of the F-1035 film prepared from target A were in general agreement with the values obtained by x-ray analysis for K, Ca, and Fe and were 2 percent, 21 percent, and 5 percent, respectively.

TABLE 5. ANALYSIS OF GLASS FILMS FROM SPUTTERING TARGET A (INSTRUMENT MIN/TIA5.5)

WEIGHT PERCENT FOUND

Sample Sequence	Sample	% SiO ₂	% CaO	% K ₂ O	% Fe ₃ O ₄	Wt. of Glass Film, μ g	Total Mass μ g/cm ²	Sputtering Time (hrs)
1	F-1035	32.7	17.9	3.0	7.4	2,070	367	17
2	F-4	52.6	19.9	4.8	9.3	997	177	6
	F-5	49.0	19.0	4.5	8.7	1,059	188	
	F-6	51.1	19.3	4.7	9.0	1,012	179	
	Average	50.9	19.4	4.7	9.0			
3	F-11	54.3	18.2	4.7	8.8	688	122	3
	F-12	50.9	16.9	4.5	8.2	702	124	
	F-13	53.7	18.0	4.7	8.7	685	121	
	Average	52.9	17.7	4.6	8.6			
4	F-7	38.9	18.5	2.7	7.3	1,604	284	9
	F-9	39.8	19.2	2.8	7.5	1,582	280	
	Average	39.4	18.9	2.75	7.4			
Nominal Values of Bulk Glass:		36.0	18.0	10.0	13.5			

TABLE 6. ANALYSIS OF GLASS FILMS FROM SPUTTERING TARGET B (INSTRUMENT MIM/TLA5.5)

WEIGHT PERCENT FOUND

Sample Sequence	Sample	% SiO ₂	% CaO	% ZnO	% PbO	Wt. of Glass Film, μg	Total Mass $\mu\text{g}/\text{cm}^2$	Sputtering Time (hrs)
1	F-17	38.5	34.6	7.3	8.3	1,568	278	6
	F-19	37.4	33.4	7.0	7.8	1,583	281	
	Average	38.0	34.0	7.2	8.1			
2	F-23	50.9	35.3	9.5	9.5	692	123	3
	F-24	47.7	33.2	9.5	9.4	679	120	
	F-25	50.5	35.0	9.6	9.4	678	120	
	Average	49.7	34.5	9.5	9.4			
3	F-20	43.0	31.8	7.3	8.4	583	103	~2
	F-21	45.4	32.9	8.6	9.5	561	99	
	F-22	42.6	31.2	7.6	8.6	613	109	
	Average	43.7	32.0	7.8	8.8			
Nominal Values of Bulk Glass:		36.0	18.0	20.0	26.0			

In summary, the results show a sizable variation in the elemental composition of these glass films as compared with the bulk glass using the model MIM/TLA 5.5 instrument. Reasonable agreement between the bulk glasses and the films prepared from target A was obtained for some elements (e.g., Si and Ca) only for the longest sputtering times. This suggests that the deposition rate or sputtering rate is not sufficient for the establishment of conditions in which the rate of production and/or deposition of sputtered atoms is constant. The operational parameters for sputtering were maintained nearly identical for all the glass films prepared and presented in TABLES 5 and 6. The sputtering rate was approximately 15-20 Å/min.

Although a sizable variation was noted in the film composition compared to the bulk glass composition, glass films produced in this manner can still be potential standard reference samples provided that the film composition obtained from any particular target is reproducible. Therefore, a series of experiments was performed in which instrumental parameters, such as ion-acceleration voltage, and ion-beam current, were systematically varied to determine their effect on the elemental composition of the glass films. At the same time, it was of interest to determine if the differences in the film vs. the bulk glass composition could be minimized with further modifications in the technique.

6. GLASS FILM COMPOSITION STUDIES B

We have focused on two possible causes for the observed differences shown in TABLES 5 and 6 between the film and bulk glass target compositions. First, localized heating of the glass target surface in the model MIM/TLA 5.5 instrument due to ion beam bombardment can cause diffusion of compounds deeper into the glass target and away from the surface. Secondly, when compounds are being removed from the target by sputtering, metal-to-oxygen bonds can break so that metal atoms rather than the metal oxides are collected on the substrate. These effects can cause the elemental concentration at the surface to change relative to the bulk concentration. With the availability of the model MIM/TLA 15 instrument, the features already mentioned removed any localized heating effects. In addition to this change, a small partial pressure of oxygen (~10-12%) was introduced into the argon atmosphere during the sputtering operation. This was done to aid the recombination with oxygen of any sputtered atoms generated at the target surface.

Comparison of the average film composition obtained with the two instruments using target B is presented in TABLE 7. It can be seen from these results that the addition of oxygen in the sputtering atmosphere produced films whose composition for Ca, Zn, and Pb was closer to the bulk glass composition. It is interesting to note that although preferential sputtering for the light elements Si and Ca, and a decrease for Zn and Pb still exists, the absolute values of the relative differences from the bulk composition are approximately the same.

TABLE 7. COMPARISON OF THE AVERAGE COMPOSITION OF SPUTTERED FILMS USING TWO DIFFERENT INSTRUMENTS (TARGET B)

Instrument	% SiO ₂	% CaO	% ZnO	% PbO
1977 Average ¹	43.7	32.0	7.8	8.8
1978 Average ²	46.4	22.9	14.5	19.5
Bulk Comp.	36.0	18.0	20.0	26.0
% Rel. Δ, ^{a,1}	+21	+78	-61	-66
% Rel. Δ, ^{a,2}	+29	+27	-28	-25

^aPercent relative difference between the film and bulk composition, i.e.,

$$\frac{\text{Film-Bulk}}{\text{Bulk}} \times 100$$

¹ --Model MIM/TLA 5.5

² --Model MIM/TLA 15

Another important result obtained by the addition of oxygen to the sputtering atmosphere was that the amount of entrapped argon in the glass film was substantially reduced. Therefore, all subsequent work was performed with 5-10% partial pressure of oxygen added to the sputtering atmosphere.

7. EFFECT OF SPUTTERING PARAMETERS ON GLASS FILM COMPOSITION

To study the effects of ion-acceleration voltage and ion-current on the film composition, six sets of polycarbonate substrates were coated with glass from target B. In TABLE 8 is a summary of the instrument conditions employed. The composition of the glass films measured by EDXRF are presented in TABLE 9. It appears from the data that varying the ion-voltage and ion-current does not affect the film composition significantly. The best agreement between sets was obtained in sets 2 and 3 which were done on the same day under identical conditions. The mass loadings of glass deposited varied from 40 μg/cm² (set 4) to 160 μg/cm² (set 5). The best measurement precision obtained was within set 5 which also corresponded to the set with the highest mass loading. The microstructures of the deposited films from target B were examined by SEM and photomicrographs of two films at mass loadings of 50 μg/cm² and 160 μg/cm² are presented in Figs. 8 and 9, respectively. In comparing the figures it can be seen that at higher glass mass loadings more of the open polycarbonate structure is filled with deposited glass and thus should be more uniform. It is also believed that the better precision at the higher mass loadings is due to the greater mass difference between film and substrate which can be measured gravimetrically with greater accuracy and precision. The amount of glass deposited at 160 μg/cm² loading corresponds to about 1.0 mg and can be measured with an accuracy of ± .01 mg. To obtain

TABLE 8. SUMMARY OF SPUTTERING CONDITIONS EMPLOYED^a

Date	Set No.	No. in Set	Time hrs.	Filament	Plasma Generator	Ar mm Hg	O ₂ mm Hg	Ion- Accl. Voltage	Neutralizer	Ion- Current	Ion Focus
5/4/78	1	3	4.2	16-24.5/5.5	60/2.6	7x10 ⁻⁵	1x10 ⁻⁵	700-800	46/2.6	45 mA	90/40
5/5/78	2	7	4.4	16-24.5/5.5	60/2.6	7x10 ⁻⁵	1x10 ⁻⁵	700-800	46/2.6	45 mA	90/40
5/5/78	3	6	4.3	16-24.5/5.5	60/2.6	7x10 ⁻⁵	1x10 ⁻⁵	700-800	46/2.6	45 mA	90/40
6/19/78	4	5	2.5	16-24.5/5.5	60/2.6	7x10 ⁻⁵	1x10 ⁻⁵	1,000	46/2.6	85 mA	90/40
6/26/78	5	5	3	24.5/5.5	60/2.6	7x10 ⁻⁵	1x10 ⁻⁵	1000-1500	46/2.6	119 mA	90/40
6/29/78	6	5	3	16/5.2	90/.78	7x10 ⁻⁵	1x10 ⁻⁵	1,500	46/2.6	70 mA	150/10

^aInstrument Model MIM/TLA 15

TABLE 9. COMPOSITION OF GLASS FILMS DETERMINED BY
EDXRF

(Target B)

Set No.	No. In Set		% SiO ₂	% CaO	% ZnO	% PbO
1	3	AV.	48.7	21.4	14.5	21.2
		S _x ^a	3.0	1.2	0.5	0.7
2	7	AV.	46.6	22.4	14.9	20.8
		S _x	1.0	0.5	0.3	0.5
3	6	AV.	46.4	21.7	14.7	20.3
		S _x	1.1	0.4	0.3	0.4
4	5	AV.	43.5	22.4	14.2	18.4
		S _x	0.9	0.5	0.3	0.3
5	5	AV.	45.6	23.8	13.3	16.7
		S _x	0.2	0.1	0.1	0.1
6	5	AV.	47.5	25.4	15.4	19.5
		S _x	0.6	0.3	0.2	0.2
Overall Average			46.4	22.9	14.5	19.5
		S _{AV} ^b	0.7	0.6	0.3	0.7
Bulk Comp.			36.0	18.0	20.0	26.0

^aS_x is one standard deviation of the average value of each set (i.e., $S/\sqrt{n}$) where S is the standard deviation of a single measurement.

^bS_{AV} is one standard deviation of the overall average of all the sets (i.e., n = 31).

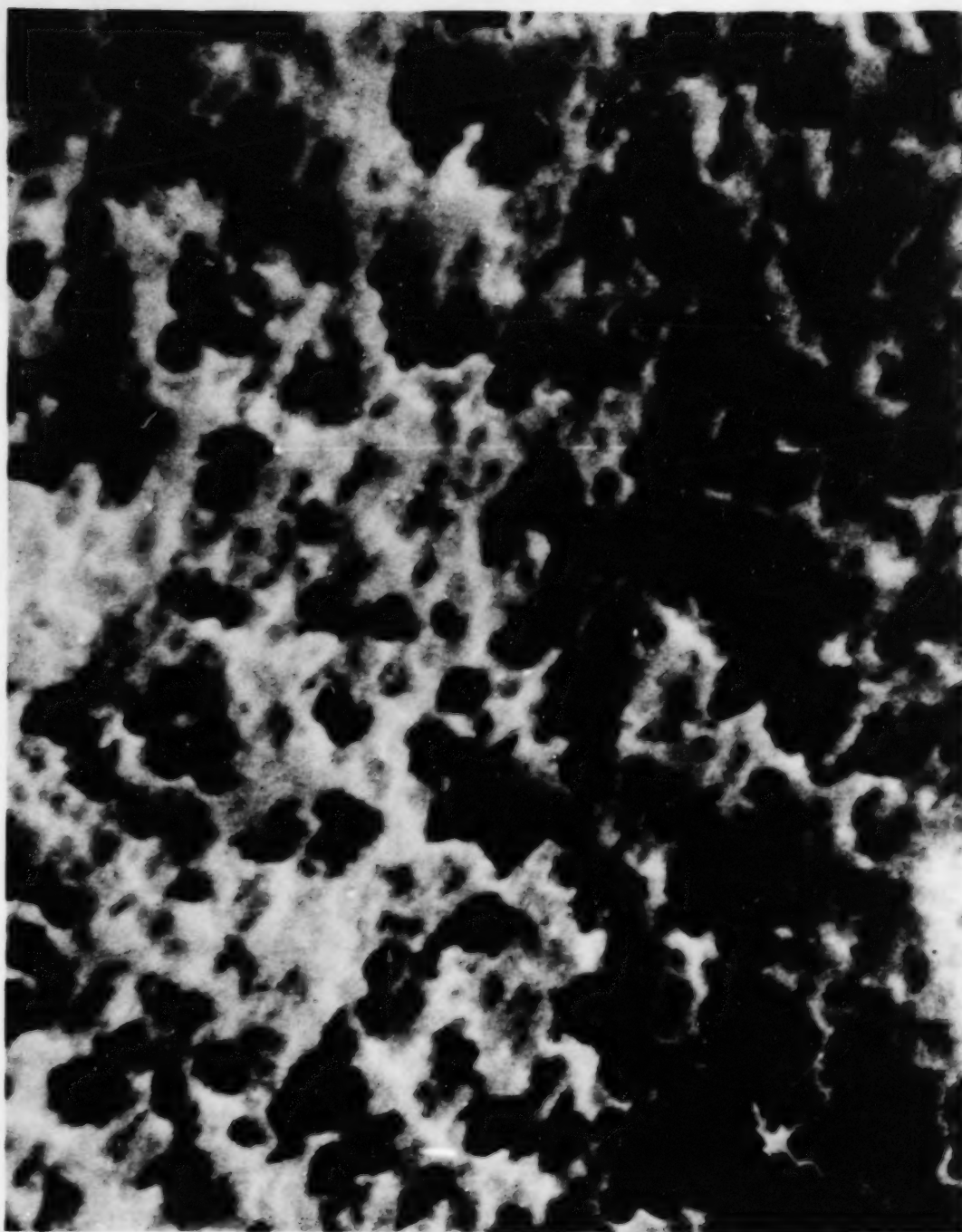


Figure 8. SEM photo of target B film: Mass loading = $50 \mu\text{g}/\text{cm}^2$.



Figure 9. SEM photo of target B film: Mass loadings = $160 \mu\text{g}/\text{cm}^2$.

more information at the higher mass loadings three additional sets were prepared where the sputtering time was about 5 1/2 hours each with identical sputtering parameters. The mass loading varied from 167 to 185 $\mu\text{g}/\text{cm}^2$. These results are tabulated in TABLE 10. It can be seen from the data that the within set precision is again comparable to that found for set 5 in TABLE 9, and corresponds to a R.S.D. of the mean of 0.7% for SiO_2 , 0.8% for CaO , 2% for ZnO , and 1.3% for PbO . The maximum variation between sets for each element in TABLE 10 is on the order of 10% for SiO_2 , 6% for CaO , 7% for ZnO , and 7% for PbO . The maximum variation between sets for each element in TABLE 9 is 12% for SiO_2 , 19% for CaO , 16% for ZnO , and 27% for PbO . Hence it can be concluded that variations in sputtering parameters does not seem to affect the SiO_2 composition but does introduce two to three times more variability for Ca , Zn , and Pb . In addition, good film reproducibility within sets was obtained with glass mass loadings from 160-190 $\mu\text{g}/\text{cm}^2$.

In Figures 10 and 11 are EDXRF spectra of glass films produced from targets C and D. The mass loading of the glass films in Figures 10 and 11 are approximately 73 $\mu\text{g}/\text{cm}^2$ and 122 $\mu\text{g}/\text{cm}^2$, respectively. These results indicate that sulfur- and phosphorus-containing glass films can be fabricated by this sputtering technique. Such films, however, would require relatively large x-ray absorption corrections for sulfur and phosphorus because of the absorption by the glass film matrix. These corrections, however, can in principle be determined. For example, a film about 180 $\mu\text{g}/\text{cm}^2$ the attenuation for sulfur assuming the glass film composition is the same as target C would be about 20%. Because of the relatively large corrections involved for sulfur and phosphorus, the targets employed for the fabrication of such films should ideally contain a minimum number of matrix elements of low atomic number. Although the composition of target C is homogeneous, the large amount of Na_2O present makes it water soluble. Therefore, films produced from it are moisture sensitive. Current research efforts are being directed toward fabricating a low atomic number glass composition containing sulfur which is less moisture sensitive. Target D, on the other hand, appears suitable for fabricating moisture-resistant phosphorous-containing films.

8. RADIAL COMPOSITION OF GLASS FILMS

Another experiment was performed to characterize the radial film composition of the glass films across the diameter of the new 15.3 cm substrate holder designed to hold up to eight substrates in the MIM/TLA 15. The same geometry as shown in Figure 2 was used except a vertical 23 cm strip holder was fastened to the substrate holder and mounted vertically and parallel with respect to the target. This stationary vertical strip held five 37 mm substrates, three within the 15.3 cm diameter of the substrate holder and two outside as shown in Figure 12. The substrates were numbered consecutively as shown in the figure. Target B was sputtered for about five hours and the resultant films were analyzed by EDXRF as described previously. The data obtained are summarized in TABLE 11.

TABLE 10. COMPOSITION OF GLASS FILMS AT HIGHER MASS LOADINGS^a
(Target B)

Set No.	Film No.	Mass Loading Glass Film $\mu\text{g}/\text{cm}^2$	% SiO_2	% CaO	% ZnO	% PbO
1	1	180.4	43.1	23.3	12.8	16.6
	2	184.0	42.1	22.7	12.3	16.1
	3	184.2	41.5	22.5	12.4	16.0
	4	181.0	43.6	23.5	12.5	16.7
	5	179.6	43.4	23.3	12.8	16.7
2	AV.	—	—	—	—	—
	S _x ^b	—	0.4	0.2	0.1	0.2
	1	179.4	45.4	24.5	12.6	15.7
	2	178.0	45.0	24.4	12.6	15.7
	3	185.4	44.9	23.7	11.9	15.0
3	4	178.8	44.7	24.0	12.5	15.5
	AV.	—	—	—	—	—
	S _x	—	0.2	0.2	0.2	0.2
	1	167.1	47.0	24.9	12.4	15.4
	2	170.0	47.4	24.8	11.5	15.2
3	3	182.6	46.2	24.0	11.2	15.2
	4	173.2	47.2	24.4	11.5	15.1
	AV.	—	—	—	—	—
	S _x	—	0.3	0.2	0.3	0.1

^a Ion-acceleration voltage = 1000V; Ion-current = 90mA; Time = 5 1/2 hours.

^b Standard Deviation of the mean value i.e., $(S/\sqrt{n})$ where S is the standard deviation of a single measurement.

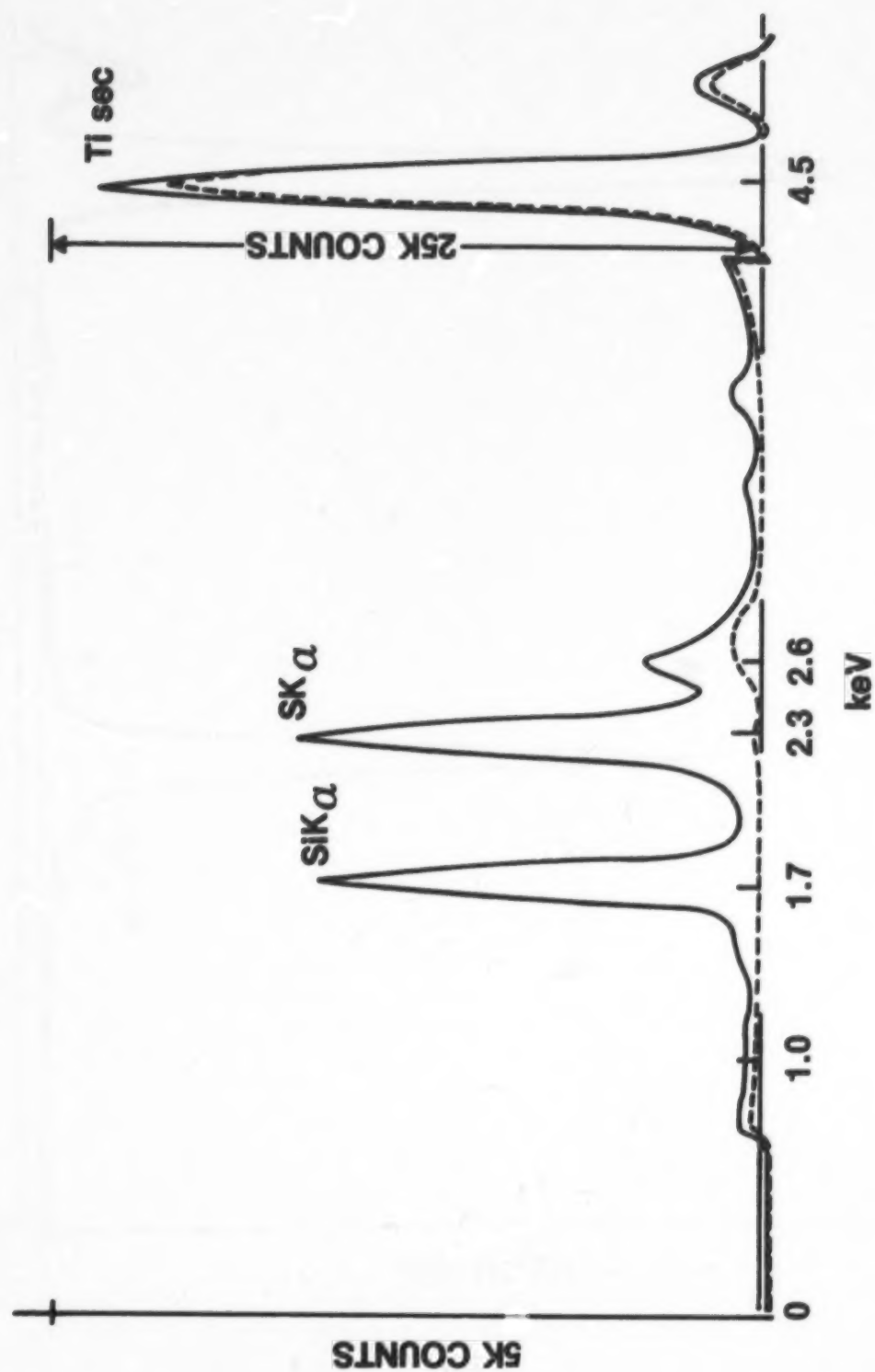


Figure 10. EDXRF spectrum of film from target C.

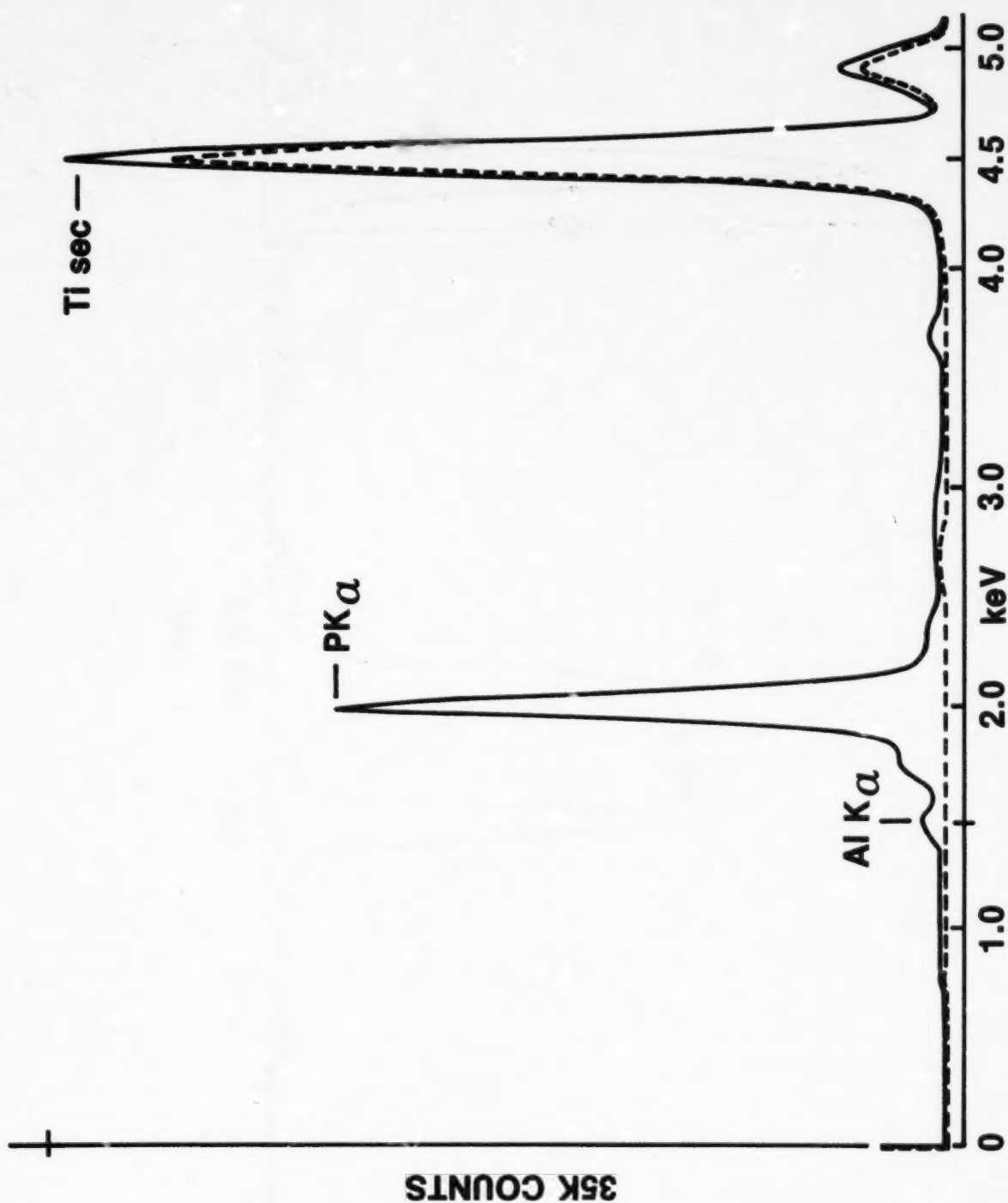


Figure 11. EDXRF spectrum of film from target D.

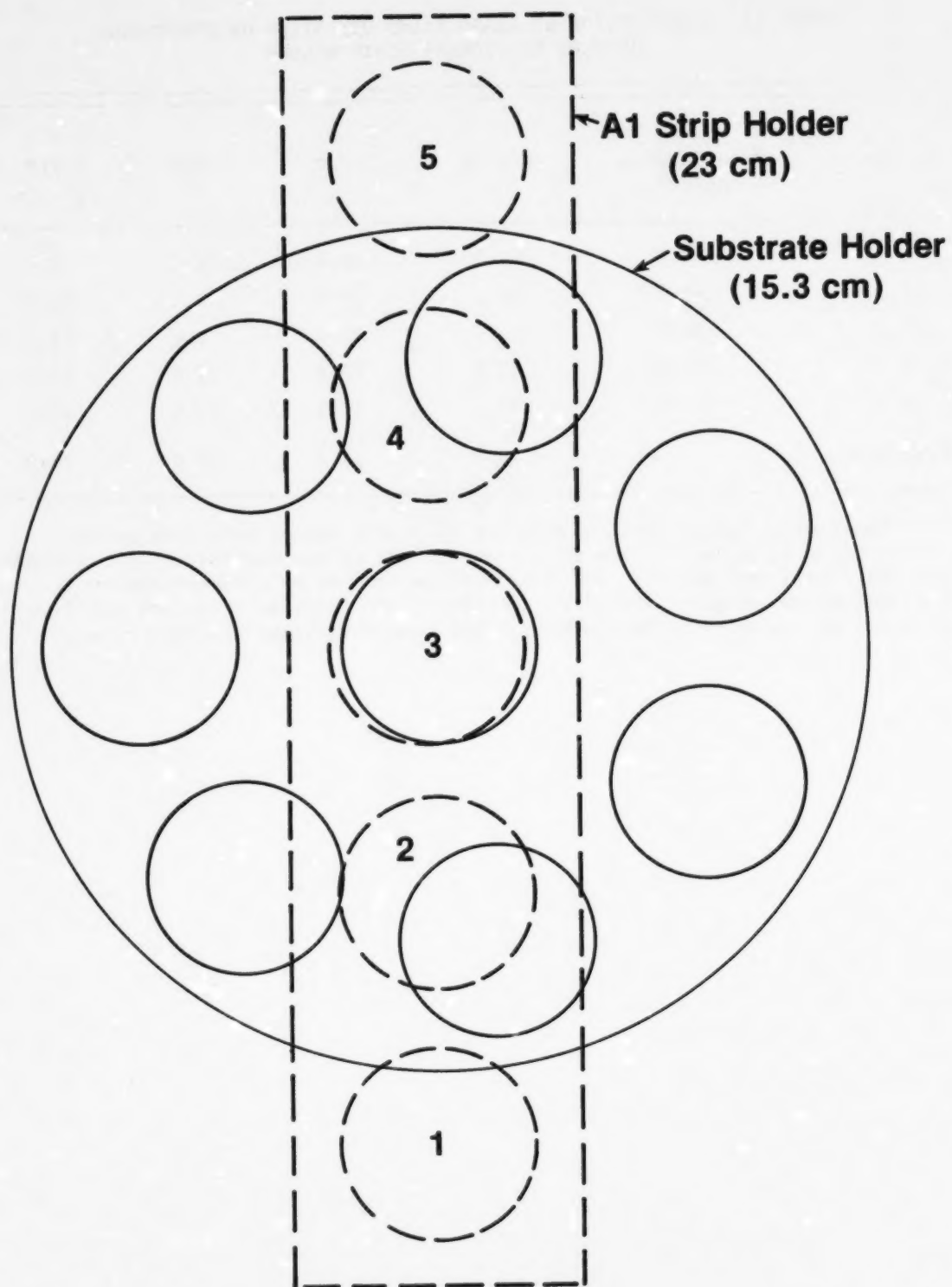


Figure 12. Al strip holder.

TABLE 11. COMPOSITION OF GLASS FILMS DEPOSITED ON SUBSTRATES
HELD BY STATIONARY STRIP HOLDER

Film #	Glass Mass Loading $\mu\text{g}/\text{cm}^2$	% SiO_2	% CaO	% ZnO	% PbO
1	160.0	41.5	25.0	8.0	9.0
2	169.0	44.1	26.7	9.7	12.2
3	180.0	40.4	23.0	9.6	13.9
4	161.0	42.9	22.6	11.3	17.5
5	144.0	39.1	17.1	10.4	17.6
Bulk Comp., %		36.0	18.0	20.0	26.0

These data suggest that within the 15.3 cm diameter substrate holder (i.e., films 2, 3, and 4) the glass composition is not significantly different for SiO_2 , CaO , and ZnO , but for PbO there appears to be a concentration gradient which is quite marked especially if one includes films one and five. Rotation of the substrates, however, will tend to average out this effect.

9. SUPPLEMENTARY STUDIES

A. Thin Metal Films Prepared by Thermal Evaporation

To assess the state-of-the-art for producing thin films of metals thermally evaporated on polycarbonate substrates, a few selected thin films were purchased from a commercial supplier and characterized. These consisted of Ti, Fe, Pb, and Zn, each at three mass loadings ranging from 50 to 100 $\mu\text{g}/\text{cm}^2$. We have characterized these films by independently measuring the mass loading at NBS by gravimetry and by x-ray fluorescence spectrometry.

1. Mass Loading Measurements

A number of filters preweighed at NBS were sent to Micromatter Co. for coating with high purity Ti, Fe, Pb, and Zn. These metals were chosen because they cover a large range in atomic number. Three films of each metal from 50 to 180 $\mu\text{g}/\text{cm}^2$ were deposited on these substrates by thermal evaporation. A film of gold was also deposited on a preweighed filter to serve as a control. The mass loading of each metal was determined at Micromatter by weighing. The filters were mounted on removable lucite rings and returned to NBS. A comparison of the mass loadings as determined by Micromatter and NBS are presented in TABLE 12. As seen from the table, the best agreement between the two laboratories was obtained with the Ti films. With both the lead and zinc films, the NBS results were systematically higher. This is probably due to oxidation of the metal films after removal from the evaporation chamber which continues for a considerable time after leaving the Micromatter Co. This points out the difficulty in obtaining independent accurate mass loading measurements to better than five percent by gravimetric means which is the simplest and least expensive method. It can be seen from the data that in order to obtain an accuracy of better than five percent in the mass loading by gravimetric methods, additional precautions must be taken. For easily oxidizable metals, the weighing should preferably be done in situ or alternatively by protection of the evaporated film in an inert environment prior to and during the weighing operation. Some laboratories have balances incorporated in vacuum systems but these are few, and it is a relatively expensive proposition for commercial suppliers to build such systems.

TABLE 12. COMPARISON OF MASS LOADINGS OF VARIOUS METAL FILMS
ON POLYCARBONATE SUBSTRATES BY GRAVIMETRY

Sample	Micromatter μg	NBS μg	Percent Difference
Blank Filter	7,882	7,878	- 0.05
Au Deposit	676	693	+ 2.5
#1 Pb	458	505	+ 9.0
#2 Pb	701	753	+ 7.0
#3 Pb	375	405	+ 8.0
#1 Fe	377	352	- 6.6
#2 Fe	968	1,003	+ 3.5
#3 Fe	724	691	- 5.0
#1 Ti	491	510	+ 4.0
#2 Ti	407	402	- 1.3
#3 Ti	732	730	- 0.3
#1 Zn	248	280	+12.0
#2 Zn	906	930	+ 3.0
#3 Zn	614	651	+ 6.0

2. X-Ray Fluorescence Measurements

The above films were mounted between two flat lucite rings and measured with EDXRF. The x-ray fluorescence measurements did not reveal appreciable amounts of any elements in the films other than the element of interest. The net intensities of the Ti K α , Fe K α , Zn K α , and Pb L α were measured. In TABLE 13 is a summary of the net intensity of each film divided by the mass loading (Micromatter values) in $\mu\text{g}/\text{cm}^2$. Since the x-ray fluorescence intensity is directly proportional to the mass loading for these thin films, the ratio of intensity to mass loading should be a constant. The estimated standard deviations of each set were also calculated and are included in the table.

From TABLE 13, the variability of the Ti, Fe, and Pb films are comparable, but again the largest variation was noted with the zinc films. The conclusion of this limited study is that there may exist some serious problems in obtaining accurate mass loadings of some thermally deposited metal films.

TABLE 13. RATIO OF INTENSITY TO MASS LOADING (I/M) FOR Zn, Pb, Fe, AND Ti FILMS
(s = standard deviation of a single measurement)

Sample	I/M (counts/ $\mu\text{g}/\text{cm}^2$)
#1 Ti	159
#2 Ti	156
#3 Ti	149
Average	= 155
s	= 5.1 (3.3%)
#1 Fe	420
#2 Fe	399
#3 Fe	414
Average	= 411
s	= 10.8 (2.6%)
#1 Pb	37.2
#2 Pb	39.9
#3 Pb	38.6
Average	= 38.6
s	= 1.4 (3.5%)
#1 Zn	884
#2 Zn	722
#3 Zn	901
Average	= 836
s	= 99 (12%)

B. Thin Aluminum Foils

Some materials which are already commercially available can serve as thin calibration standards provided that their trace element composition can be measured. Four square sections ($\sim 5 \text{ cm}^2$) from a commercial aluminum foil ($6.3 \mu\text{m}$, $\sim 2 \text{ mg/cm}^2$) have been examined for homogeneity by EDXRF. The elements Fe and Ga were examined at approximately the $6 \mu\text{g/cm}^2$ (3000 ppm) and $0.1 \mu\text{g/cm}^2$ (50 ppm) levels, respectively. The estimates of relative standard deviations of a single measurement for Al, Fe, and Ga based on four sections of foil were less than 3.0 percent. Although this material seems homogeneous, it does appear that thin Al foils would find few applications as a calibration standard because of the limited choice of elemental constituents.

C. NBS-SRM 1648 Urban Particulate Deposited on Membrane Filters

We have attempted to deposit NBS-SRM 1648 Urban Particulate on membrane filters to serve as a potential thin calibration standard using essentially the same procedure developed for depositing reground orchard leaves (3). We found, however, that many of the particles tended to clump together rather than disperse uniformly on the filters. For this reason, this work was discontinued. It appears that materials of this type may be deposited more uniformly with an air filter facility as described by Olson (10), but this may require reanalysis of the deposited material.

D. Synthetic Ground Glasses Deposited on Filters

Another type of potential synthetic particulate standard was investigated and consisted of synthetic ground glass of known particle size deposited on membrane filters. We have investigated three types of grinders in order to reduce the particle size below $2 \mu\text{m}$. These consisted of grinding in (a) an alumina ball mill, (b) a "puck and ring" commercial mill, and (c) a commercial automated mortar and pestle apparatus. A sedimentation procedure was used to separate the fine particles from coarser ones greater than $2 \mu\text{m}$. Although this resulted in the separation of a large fraction of particles below about $5 \mu\text{m}$, it is difficult to obtain a size distribution where 95-100% of the particles are below $2 \mu\text{m}$. One major problem with grinding is that elemental contamination can easily be introduced although this would be minimized using boron carbide grinding materials.

Results obtained thus far on the ground synthetic classes demonstrate that such a particulate thin standard is feasible. Additional work is required to obtain a sufficient supply of glass particles small enough for deposition on membrane filters. The size, of course, is critical in order to minimize particle-size x-ray absorption effects. In addition, to obtain sample integrity a suitable adhesive would be necessary to keep the glass deposit fixed to the substrate. Binding of the deposit to the filter with a collodion film layer as described by Semmlar et al. (11) may be appropriate and will require further investigation.

10. CONCLUSION

From evaluation of the results obtained multi-element thin standards suitable for calibration purposes can be fabricated by the focused ion-beam

sputtering technique. In order to include all the elements of interest in any particular film, several glass targets would need to be fabricated. Because there exists a difference in the film composition compared to the bulk target, the elemental composition of these films can be measured and certified by NBS using x-ray spectrometric and other instrumental analysis techniques.

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